Supplementary Material

Effects of Molecular Size and Orientation on Interfacial Properties and Wetting Behavior of Water/n-Alkane Systems: A Molecular-Dynamics Study

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1 Force Fields

In this study, we use a rigid water model (TIP4P-2005) constructed by Abascal et. al. based on the same geometry of the original TIP4P.[1] It contains four sites of interactions, one of them is placed at the oxygen position and two at the hydrogen atom positions. The fourth site, often called the virtual M site, is located at the bisector of the H–O–H angle. The transferable potentials for phase equilibria-united atom (TraPPE-UA) force field is used for the n-alkane systems.[2–5] In the TraPPE-UA force field, methyl and methylene are treated as pseudoatoms located at the sites of the carbon atoms. The force field parameter values of TIP4P-2005 and TraPPE-UA are listed in Table S1. The strength of interaction between TIP4P-2005 oxygen atom and TraPPE methyl/methylene groups of Heptane is tuned using the equation $\varepsilon_{OC} = (1+r)\sqrt{\varepsilon_O \varepsilon_C}$. The optimal interaction strengths of water/n-alkane ε_{OC} for the methyl and methylene groups are found at $r = 0.12$ to be $\varepsilon_{OC} = 0.88997$ and $\varepsilon_{OC} = 0.609728$, respectively. Theses values are used for all water/n-alkane (nC5-nC16) systems.

Table S1 Bonded and Nonbonded Parameters for TIP4P-2005 and TraPPE-UA Force Fields.

Non-Bonded Parameter				
Atom	Mass [amu]	Charge $[e]$	σ_{LJ} $[nm]$	ε_{LJ} $[kJ\ mol^{-1}]$
TIP4P-2005				
O	15.9994	0.00	0.31589	0.7749
H	0.00	0.5564	0.00	0.00
M	0.00	-1.1128	0.00	0.00
TraPPE-UA				
CH_2	14.027	0.00	0.395	0.38246
CH_3	15.035	0.00	0.375	0.81482
Bonded Parameter				
Stretch	$r_b[nm]$	Bend	θ [deg]	$k_\theta[kJ\ mol^{-1} rad^{-2}]$
O-H	0.09572	H-O-H	104.52	628.02
O-M	0.01546			
CH_x-CH_y	0.154	CH_x-(CH_2)-CH_y	114.0	519.7
Torsion	C_1 $[kJ\ mol^{-1}]$	C_2 $[kJ\ mol^{-1}]$	C_3 $[kJ\ mol^{-1}]$	C_4 $[kJ\ mol^{-1}]$
CH_x-(CH_2)-(CH_2)-CH_y	5.904	-1.1339	13.159	0.00

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2 Results and Error Analysis

In this work, we apply molecular dynamic simulations (MD) to study the interfacial properties of water/n-alkane using the TIP4P-2005 and TraPPE-UA force fields at $T = 295\ K$. The results of pure n-alknae, pure water, and water/n-alkane interfacial tensions, and contact angle are listed in table S2. The standard errors of the mean from 150 ns of MD simulations time ($\delta\gamma_{wv}$,$\delta\gamma_{av}$,$\delta\gamma_{wa}$) are used to calculated the uncertainties associated with contact angles ($\delta\theta_c$) as[6]

$$\delta\theta_c = \frac{\sqrt{\gamma_{wv}^2\delta\gamma_{wv}^2 + (\gamma_{av} + \gamma_{wa}\cos\theta_c)^2\delta\gamma_{av}^2 + (\gamma_{wa} + \gamma_{av}\cos\theta_c)^2\delta\gamma_{wa}^2}}{\gamma_{av}\gamma_{wa}\sin\theta_c} \qquad \theta_c \neq 0. \tag{1}$$

The simulation results of water/n-alkane contact angles are compared (Figure 5 in the corresponding paper) with those calculated from the experimental values of water surface tension ($\gamma_{wv} = 72.52$ mN/m)[7] and the experimental values of γ_{wa} and γ_{av} (table.S3).[8]

Table S2 MD results of interfacial tension (in unit of mN/m) and contact angle values of water/n-alkane interfaces.

C_N	γ_{wv}	γ_{av}	γ_{wa}	$\delta\gamma_{wv}$	$\delta\gamma_{av}$	$\delta\gamma_{wa}$	S	θ_c[deg.]	$\delta\theta_c$[deg.]
5	69.44	46.90	16.86	0.26	0.23	0.15	5.68	0.00	
6	69.44	47.03	19.50	0.42	0.15	0.15	2.91	0.00	
7	69.44	47.65	21.45	0.47	0.21	0.15	0.34	0.00	
8	69.44	47.82	23.23	0.18	0.12	0.15	-1.62	26.12	0.04
9	69.44	48.34	24.30	0.40	0.13	0.15	-3.20	36.25	0.04
10	69.44	48.56	25.47	0.32	0.37	0.15	-4.59	42.80	0.04
11	69.44	49.16	26.17	0.25	0.21	0.15	-5.89	48.05	0.02
12	69.44	49.04	27.16	0.34	0.44	0.15	-6.76	50.92	0.03
13	69.44	48.95	28.06	0.37	0.37	0.15	-7.57	53.39	0.03
14	69.44	49.55	28.32	0.83	0.51	0.15	-8.43	56.12	0.05
15	69.44	49.58	29.03	0.51	0.48	0.15	-9.17	58.11	0.04
16	69.44	50.37	29.20	0.34	0.52	0.15	-10.14	60.89	0.03

Table S3 Experimental values of interfacial tensions and contact angles of water/n-alkane systems.

C_N	γ_{av}[mN/m]	γ_{wa}[mN/m]	S[mN/m]	θ_c[deg.]
5	15.9	50.9	5.7	0
6	18.3	51.4	2.8	0
7	20.05	51.9	0.6	0
8	21.55	52.5	-1.5	25.7
9	22.7	52.4	-2.6	32.9
10	23.7	53.2	-4.4	42.2
11	24.6	53.1	-5.2	45.4
12	25.3	53.7	-6.5	50.3
13	25.95	54	-7.4	53.4
14	26.4	54.5	-8.4	56.4
16	27.2	55.2	-9.9	60.6

Notes and references

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